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RARE-EARTH PICOLINATE AND PICOLINATE-N-OXIDE COMPLEXES

by

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Stepwise stability constants for rare-earth picolinate and rare-earth picolinate-N-oxide complexes (Figure 1) have been reported in two recent publications (1, 2). The n-dentate characters of the two ligands were discussed, but no unequivocal conclusions were drawn.

It has been shown in earlier publications (3, 4) that the magnitudes of ratios (P) of stepwise stability constants are useful in elucidating the structures of metal complexes, and in this paper the P values for the picolinate and picolinate-N-oxide systems are analyzed. The stepwise stability constant is defined as

$$b_m = \left[ML_m\right] \Big/ \left[ML_{m-1}\right]\left[L\right] \quad ,$$

where M and L are metal and ligand ions respectively. The ratios are given by

$$b_1 : b_2 = P = S \times T \times R,$$

where S is a statistical factor calculable from a knowledge of the number

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of available cation sites and ligand groups, T is a measure of the electrostatic repulsion between the bound ligand (in ML_1) and the ligand about to bind (L_2), and R covers any change in the nature of the metal–ligand bonding in the first and second stages of ion association. The S, T, and R factors have been described in detail in earlier publications (3, 4). For the α-hydroxymonocarboxylate complexes of rare-earth, cupric, and zinc ions T = 1.6 and R = 1.0 (3), and it was postulated that a T value = 1.6 is valid for singly-charged ligands binding to transition metal or rare-earth ions. This T value also holds for some transition metal halide and amino acid complexes (5).

P values for the presently studied systems may be calculated in the following manner. For a monodentate ligand binding to a 6-coordinate rare-earth ion S = 2 x 6/5 = 2.40. Table I lists P, S, and T values for monodentate and bidentate ligands associating with 6- and 8-coordinate cations. The experimentally determined P values are listed in Table II.

The P(calc.) and P(obs.) are indicative of a monodentate picolinic acid-N-oxide. The pK_a value (3.31) for this ligand is of the same order as the pK_a values for the α-hydroxymonocarboxylin acids studied earlier. For a much weaker acid, however, the metal–ligand bond may have a lifetime greater than that of a metal–water bond, and chelation would then occur. The P(obs.) values for the picolinic acid (pK = 5.34) complexes are consistent with bidentate ligandcy (Tables I and II). Thompson's (1) P(obs.) values indicate an 8-coordinate cation while the data of Yoneda and

coworkers (2) support a 6-coordinate structure. If we omit the two "wild" P(obs.) values for Ce and Lu picolinates, as determined by Yoneda and coworkers (2), the P(obs.) and P(calc.) values are in good agreement. Thompson's (1) data are extremely consistent, however, so that an unequivocal decision as to the coordination number of rare-earth ions cannot be reached. It is apparent, nevertheless, that the independent derivation of P values for the picolinate system should resolve the argument.

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TABLE I

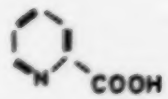
Calculation of P values

	6-coordinated		8-coordinated	
	Monodentate ligand	Bidentate ligand	Monodentate ligand	Bidentate ligand
S	2.4	4.8	2.3	3.5
T	1.6	1.6	1.6	1.6
P	3.85	7.7	3.7	5.6

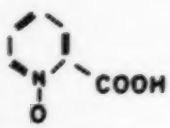
TABLE II

Log P(obs.) values for rare- earth complexes

Metal	Picolinate (1)	Picolinate (2)	N-oxide (2)
La	0.80	1.11	0.77
Ce	0.92	1.53	
Pr	0.74	0.99	0.49
Nd	0.84	0.93	0.76
Sm	0.70	0.86	
Eu	0.66	0.87	0.65
Gd	0.78	0.70	0.66
Tb	0.68		
Dy	0.70	0.74	0.45
Ho	0.72		
Er	0.70		
Tm	0.74	1.14	0.47
Yb	0.74	0.90	0.55
Lu	0.70	1.43	0.64
Average P(obs.)	5.2	10	4.0



Picolinic acid



Picolinic acid - N - Oxide

Figure I.